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**Title**
CATALYTIC BIOMASS LIQUEFACTION

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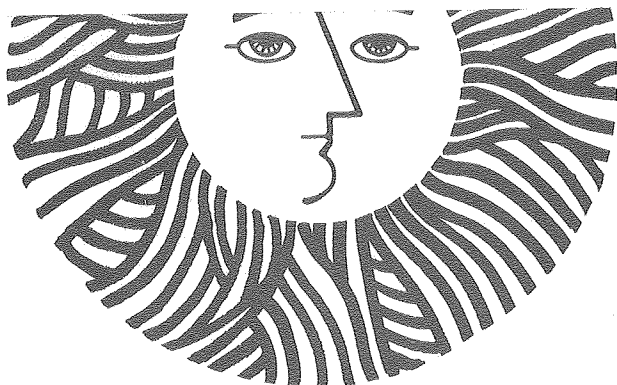## UNIVERSITY OF CALIFORNIA

# ENERGY & ENVIRONMENT DIVISION

CATALYTIC BIOMASS LIQUEFACTION

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Cihan Karatas, Larry Schaleger, Manu Seth,
James Wrathall, Nasser Yaghoubzadeh and Gary Yu

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## DISCLAIMER

CATALYTIC BIOMASS LIQUEFACTION

QUARTERLY REPORT

Thermochemical Conversion
Biomass Energy Systems Branch
Department of Energy

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# 1. INTRODUCTION

Our previous quarterly report detailed progress made on three major fronts: 1. preparation of biomass slurries; 2. characterization and flow properties of concentrated slurries; 3. construction of a biomass liquefaction process evaluation unit. This past quarter the emphasis was on: 1. characterization of product oil with a view towards possible end uses; 2. exploratory studies on solvolytic depolymerization as an alternative to hydrolytic pretreatment; and 3. ongoing engineering development in connection with readying a tubular reaction system for continuous operation.

# 2. CHEMICAL CHARACTERIZATION OF THE PRODUCTS OF WOOD LIQUEFACTION

This work was initiated before crude, wood oil from Albany test run TR-7 (October 1979) became available. A sample of product from Albany test run TR-4, conducted in May, 1979, was separated into neutral and phenolic fractions by solvent extraction according to the following scheme:

Crude Oil in MiBK

Extract with 10% Aqueous NaOH

MiBK — Neutral Fraction

Aqueous — Sodium Phenolates

1. Neutralize with HCl
2. Extract with MiBK

MiBK — Phenolic Fraction

Aqueous — Inorganic Salts + Trace Amounts of Water-Soluble Organics
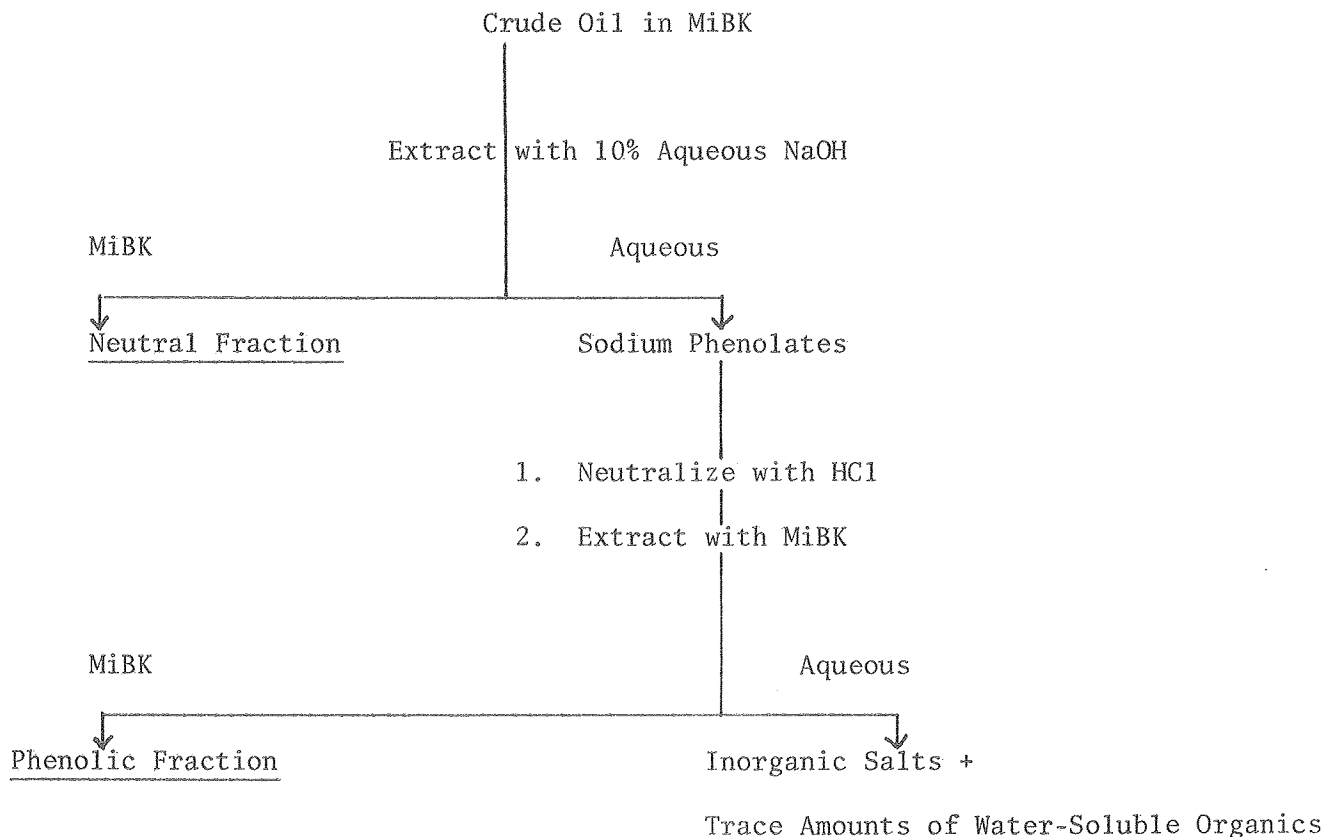
MiBK = Methyl isobutyl ketone, $CH_3COCH_2CH(CH_3)_2$

Roughly half of the crude oil was extracted into aqueous sodium hydroxide. The so-called phenolic phase was shown to contain guaiacol and propyl-guaiacol, along with many unidentified components, by GC-MS (gas chromatography - mass spectrometry) analysis. Guaiacol and propylguaiacol are phenols derived from the lignin of softwoods. The neutral phase contained species such as anthracene and phenanthrene derived not from wood but almost certainly from the anthracene oil used as a carrier solvent in the PERC process. Thus the earlier observation made by Battelle-PHN that the oil from run TR-4 appeared to be contaminated with residual anthracene oil from a previous run in the PERC mode has been confirmed. The above extraction scheme will next be applied to crude wood oil from TR-7. Efforts will be made to perfect the extraction scheme and to quantitate the results.

## 3. NOVEL PROCESS CONCEPTS

### 3.1 Liquefaction of hydrolyzed Slurry

Rapid heating of hydrolyzed slurry in a gas-fired preheater is an economically attractive and commercially viable option for large scale liquefaction plants. The rate of heat-up in conventional batch reactors is limited by their high heat capacities. In order to circumvent this problem, we have designed, fabricated and put into operation a tubular reactor bomb apparatus. Reaction tubes (1/2" dia. x 6" long) fitted with a thermocouple and pressure gauge are charged with hydrolyzed slurry, catalyst and reducing gases. A loaded tubular bomb is attached to an electro-magnetic vibrator and immersed in a hot molten salt bath. The bath, preheated to a few degrees above reaction temperature, enables the reactor contents to be heated to $360^{\circ}C$ within about 2 min. The reactor is held at temperature for the desired reaction time and then removed from the bath and quenched to room temperature by immersion into cold water. Reaction gases are vented from the cold bomb and the products washed out with acetone. The acetone slurry of the product is passed through a dry, pre-weighed thimble. The contents of the thimble are extracted with acetone in a Soxhlet apparatus, and the solvent evaporated to obtain an acetone-soluble and an acetone-insoluble fraction.

During the quarter the tubular reactor bomb system was put into operation and several runs were made using hydrolyzed slurry and mixtures of wood flour and water. Acetone-soluble and acetone-insoluble yields were found to be reproducible within 3% (based on the weight of the starting wood) in repeat experiments. The small volume of the gas sample prevented accurate gas analysis.

The reaction conditions and product yields for some key experiments are summarized in Table 1. Results obtained from a typical batch autoclave run are also shown for comparison. Several interesting conclusions may be drawn from these preliminary results. The amount of gases produced from wood can be estimated from the uncollected mass (100- wt % mass recovered in Table 1). The gases produced vary from 36 to 51% by weight of the wood. In general it appears that an increase in heating time results in improved yields of acetone-soluble material.

The acetone-insoluble materials reported in Table 1 include water-soluble components of the product. In experiment RT7, the acetone-insoluble fraction was further extracted with water. About 10% by weight of the wood was found to be insoluble in both water and acetone. These units are close to those reported earlier (1) when the reaction was run in a one liter autoclave. We feel that the tubular bomb reactor system is a useful and reliable tool for evaluating the effect of reaction condition during homogeneous catalytic liquefaction of biomass. In addition to the rapid heat-up time afforded by the equipment, it is also easy to use, allowing a large amount of data to be collected in a relatively short time.

## 3.2 Solvolytic Depolymerization of Wood

The rationale, approach and experimental producedures for the solvolysis of wood flour were described in an earlier report (1). Over 80 experiments have since been completed. All these results and the associated analytical work are being compiled and evaluated and will be presented in the near future.[2] A brief description of some of the highlights of this quarter's work follows.

During this quarter we compared the solvolysis and hydrolysis of wood flour. Reactions were run in a 350-ml Parr Reactor (1) using 1:4 ratios of wood flour and carrier vehicle. Phenol, ethylene glycol, cyclohexanol and butanol were selected as representative constituents of a process recycle solvent (1). Acid concentrations ranging from 0.1 to 0.5 wt% of the carrier were tested at temperatures of 180 and 250°C. Comparative hydrolysis runs were done at the same conditions. In all experiments the product was emptied into dry, pre-weighed thimble and the contents of the thimble extracted with acetone. The fraction of the initial wood reamining as acetone-insoluble material was used as an indication of the effectiveness of the reaction.

Results of a few illustrative runs are shown in Table 2. Based on these results it appears that solvolysis in a recycle oil carrier could be used as a pretreatment step to produce a material similar to or better than product obtained from the hydrolysis of biomass. Work done at Battelle PNL and at LBL (see earlier sections of this report), indicates that derivatives of phenol and cyclohexanol are indeed produced from the

Table 1.    Reaction Conditions and Product yields from Tubular Bomb Experiments.

Charge: -    Wood Flour        1  g        OR        Hydrolyzed Slurry        4  g
             $Na_2CO_3$ solution    4  g

Fianl Reactor Temperature:    360°C                Gases: -    CO    250 psig. initial pressure
                                                               $H_2$   250 psig  initial pressure.

| Experiment No. | Feed Stock | Sodium Carbonate Wt% of aqueous solution | Heat-up time (min.) | Time of Temperature (min.) | Acetone Solubles | Acetone Insolubles | Mass Recovered |
|---|---|---|---|---|---|---|---|
| | | | | | Wt.%  o.d. Wood charged | | |
| RT3 | Wood flour + sodium carbonate solution | 4 | 2.5 | 15 | 30 | 19 | 49 |
| RT4 | Hydrolyzed Slurry (From Albany) | 4 | 2.5 | 15 | 34 | 30 | 64 |
| RT6 | Same as RT4 | 4 | 16.0 | 0 | 27 | 31 | 58 |
| RT7 | Same as RT4 | 4 | 15.0 | 15 | 29 | 23 | 52 |
| RT8+ | Wood Flour + Sodium Carbonate Solution | 4 | 42.0 | 0 | 25* | 22† | 57 |

†    This experiment was run in a one liter Autoclave  using about 50g wood flour
*    Acetone solubles include toluene-soluble fraction.
+    Acetone insolubles include water and liquor solubles (see Ref. 1)

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Table 2:   Comparative Evaluation of the Solvolysis and Hydrolysis of Wood Flour. +

(All experiments done for 1/2 hr. using 1:4 ratio of wood flour and carrier vechicle)

Hydrolysis

| Experiment No. | Reaction Temperature ($^{\circ}C$) | Carrier Vechicle (Solvent) | Acid Conc. Wt. % of Carrier | Yield of Acetone Insolubles Wt.% of starting wood |
|---|---|---|---|---|
| RP 76 | 180 | Ethylene Glycol | 0.1 | 37 |
| RP 75 | 180 | | 0.25 | 26 |
| RP 41 | 180 | | 0.5 | 4 |
| RP 82 | 250 | | 0.1 | 5 |
| | 250 | | 0.25 | N/A |
| RP 81 | 250 | | 0.5 | 4 |
| RP | 180 | Butanol | 0.1 | 39 |
| RP 49 | 180 | | 0.25 | 17 |
| RP 46 | 180 | | 0.5 | 7 |
| RP 56 | 250 | | 0.1 | 12 |
| RP 57 | 250 | | 0.25 | 27 |
| RP 58 | 250 | | 0.5 | 32 |
| RPH 1 | 180 | Water | 0.1 | 61 |
| RP 99 | 180 | | 0.25 | 56 |
| RPH 12 | 180 | | 0.5 | 47 |
| RP 100 | 250 | | 0.1 | 43 |
| RPH 6 | 250 | | 0.25 | 41 |
| RPH 17 | 250 | | 0.5 | 38 |

liquefaction of wood. It remains to be seen if the solvolysis product can be converted to liquid fuel using either sodium carbonate or some other homogeneous or heterogeneous catalyst. Another important question that remains unanswered is the amount of solvent that is consumed by condensation with the feed-stock and whether the solvent fraction can be produced in the subsequent liquefaction step. Both these questions are being addressed in a series of experiments in progress.

4. CHARACTERIZATION AND FLOW PROPERTIES OF CONCENTRATED SLURRIES
4.1 Bran-Lubbe Pump Operation
4.1.1. Efficiency vs Viscosity: Data from pumping tests using both Albany and LBL equipment indicated that pump performance is affected by the concentration, temperature, and age of the slurry, as well as by pumping pressure and rate. Pump performance can be optimized by consideration of a single slurry parameter, flow resistance. We have found that by operating the pump under conditions which provide minimal apparent viscosity (a property similar in most respects to flow resistance), the flow regime is transformed from Stokes to Reynolds flow. This transformation can be taken advantage of both to increase pump efficiency and to make the slurry amenable to the application of conventional flow-measurement devices.

4.1.2. Stroke vs. Efficiency: We reported previously that a distinct correlation exists between reciprocating pump efficiency and the flow resistance of the fluid being pumped. Efficiency was averaged across the entire stroke range of the pump to show that pump cycle time determines the fraction of the stroke chamber that is filled with each relaxation of the piston. However, efficiency is also a function of stroke. This effect derives from several factors, chief of which are the following:

1. Gas volume %
2. Differential pump pressure.

The presence of gas in the three-phase slurry produces a compressible fluid, requiring a certain fraction of total stroke movement to compress the slurry to discharge pressure. This represents the major loss in efficiency. As stroke decreases, flow rate and therefore discharge pressure also decrease; as discharge pressure approaches suction pressure, check valves begin to fail. Finally, for a given differential of discharge vs. suction pressure, a certain amount of stroke relaxation is required to bring the compressible slurry in the stroke chamber down below suction pressure. As total stroke decreases, the fraction of stroke required for this relaxation increases, leading to loss of efficiency with decreasing stroke.

What this means for the operation of the pump in the LBL liquefaction process scheme is that maximum pump efficiency will be obtained by operating the pump at the highest practicable stroke and feed temperature.

## 5. CONSTRUCTION OF BIOMASS CONTINUOUS LIQUEFACTION UNIT (CLU)

Completion of the CLU is everal months behind schedule because of funding delays and the need to incorporate additional safety and control equipment into the design. The initiation of biomass liquefaction tests now appears to be several months in the future.

However, all tests conducted to date have been satisfactory--performance specifications have been met or exceeded. The most significant test to date was conducted during the February Contractors' meeting. Water and argon gas were passed through the system at $650^{\circ}F$ and 3,000 psi; gas feed, slurry pumping and pressure let-down systems all performed well.

Mechanical and electronic over-pressurization sensors were tested and installed to provide automatic shut-off and pressure relief protection. A gas purging system for post-run oxidative decoking of the tubular reactor still needs to be installed.

During the third quarter of FY 80, a major revision of the gas feed system will be undertaken in order to provide the capability of continuously introducing three gases--CO, $H_2$ and $CO_2$--simultaneously. This system will incorporate Brooks thermal mass flowmeters to monitor the rate of flow of each gas independently.

The question of the operating parameters to be used in initial biomass liquefaction test runs has been given detailed consideration. The main operating variables are total pressure, temperature and slurry feed concentration. If any two of these are specified, then the third is fixed. The total pressure is the sum of the saturated steam pressure at the operating temperature plus the pressure due to feed gas (carbon monoxide and hydrogen). Analysis of the relationships among these variables leads to the following general conclusions:

1. An increase in molar feed gas excess will require a lower operating temperature.

2. An increase in operating pressure will allow a higher operating temperature.

3. Steam production is accompanied by a decrease in gas residence time (solids holdup).

4. An increase in feed slurry concentration must be accompanied by a decrease in operating temperature.

The slurry feed scheduled for use in the first five runs will have a total solids content of 20% and the operating pressure will be 3,000 psig. The corresponding temperature is calculated to be $641^{\circ}F$ ($338^{\circ}C$).

## 6. CONTRACT EXPENDITURES

Expenditures to date are still on target. Operating funds in the amount of $640K have been received while another $40K is due. An additional $211K is expected for FY 80 prototype (continuous liquefaction unit) modifications.


## 7. THIS QUARTER'S ACTIVITIES

During the third quarter of FY 80, the following activities will be undertaken:

- Begin characterization of chemical components of both oil and aqueous phase from Albany test run TR-7.

- Explore solvent extraction as an alternative to distillation for fractionating product oil.

- Utilize small volume tubular bomb system to further investigate this effect of operating variables on oil yield and quality under batch conditions.

- Investigate catalytic liquefaction of pre-solvolyzed wood; examine questions of solvent recovery and regeneration.

- Debug slurry flow-measuring device developed at LBL for use at low linear velocities.

- Equip CLU with an automatic gas chromatograph for unattended analysis of $CO/H_2/CO_2$ ratios of off-gas.

- Commission and test continuous liquefaction unit.


## 8. REFERENCES

8.1 "Catalytic Liquefaction of Biomass," M. Seth, R. Djafar, G. Yu and S. Ergun, Nov. 1979, LBL #10091, UC-61.

8.2 "Solvolytic Depolymerization of Wood Flour," M. Seth and G. Yu (In progress)